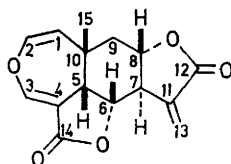


Sesquiterpenoids. Part XVIII.¹ X-Ray Crystallographic Determination of the Stereochemistry and Conformation of Miscandenin, an Elemanediolide with a Dihydro-oxepin Ring †

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The stereochemistry of miscandenin, a sesquiterpene elemanediolide, has been determined by X-ray crystal-structure analysis. The dihydro-oxepin and cyclohexane rings are *cis*-fused: the former adopts a twist-boat conformation and shows appreciable angular strain, while the latter has a distorted chair conformation. The α,γ -fused γ -lactone at C(4)—(6) adopts a slightly distorted half-chair conformation whereas the β,γ -fused γ -lactone at C(7)—(8) is closer to an envelope form in which C(7) is the out-of-plane atom. Crystals are orthorhombic, $a = 8.586(4)$, $b = 14.918(5)$, $c = 10.211(3)$ Å, $Z = 4$, space group $P2_12_12_1$. The structure was solved by direct methods from diffractometer data and the atomic parameters were adjusted by least-squares calculations which converged to R 7.0% over 1222 reflections.

THE elemanediolide miscandenin (1) was extracted from *Mikania scandens* (L.) Willd. as one of six sesquiterpene dilactones,² the other five belonging to the germacrane



(1)

class. We undertook an X-ray examination of the sesquiterpenoid in order to settle questions which arose about the previous assignment of stereochemistry² and

† No reprints available.

¹ Part XVII, P. J. Cox and G. A. Sim, preceding paper.

² W. Herz, P. S. Subramanian, P. S. Santhanam, K. Aota, and A. L. Hall, *J. Org. Chem.*, 1970, **35**, 1453.

our results help to define the stereochemistry of the biological divinylloxiran-dihydro-oxepin rearrangement implicated in the biogenesis of the sesquiterpene.^{1,3}

A non-centrosymmetric direct-method procedure was used to elucidate the crystal structure and least-squares adjustment of the atomic parameters converged to R 7.0% over 1222 independent reflections. Figure 1 illustrates the atomic arrangement in the sesquiterpenoid lactone molecule and establishes the relative stereochemistry shown in (1). Figure 2 illustrates the packing of the molecules in the crystal. Atomic co-ordinates are listed in Table 1, thermal parameters in Table 2, and bond lengths, valency angles, torsion angles, displacements of the atoms from various planes, and intermolecular separations in Tables 3—7.

In the dihydro-oxepin ring, atoms O(1), C(1), and C(3)—(5) are very closely coplanar and C(2) and C(10) are

³ P. J. Cox, G. A. Sim, J. S. Roberts, and W. Herz, *J.C.S. Chem. Comm.*, 1973, 428.

TABLE 1

Fractional atomic co-ordinates, with standard deviations

Atom	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	0.8069(7)	0.8180(3)	0.1206(6)
O(2)	0.3193(6)	0.8622(3)	0.0962(5)
O(3)	0.2893(4)	0.7452(2)	0.2285(4)
O(4)	0.3196(5)	0.3975(2)	0.0320(4)
O(5)	0.5192(4)	0.4647(2)	0.1311(3)
C(1)	0.8405(7)	0.7135(4)	0.3036(7)
C(2)	0.8848(8)	0.7747(5)	0.2217(9)
C(3)	0.6516(8)	0.8229(4)	0.1155(6)
C(4)	0.5427(6)	0.7861(3)	0.1901(5)
C(5)	0.5474(5)	0.7238(3)	0.3036(4)
C(6)	0.3888(5)	0.6764(3)	0.2854(4)
C(7)	0.4063(5)	0.6011(3)	0.1862(4)
C(8)	0.5364(5)	0.5379(2)	0.2247(4)
C(9)	0.6920(5)	0.5839(3)	0.2199(5)
C(10)	0.6903(5)	0.6623(3)	0.3198(5)
C(11)	0.2813(6)	0.5345(3)	0.1576(4)
C(12)	0.3657(6)	0.4576(3)	0.0987(5)
C(13)	0.1296(6)	0.5339(4)	0.1808(8)
C(14)	0.3789(6)	0.8044(3)	0.1615(5)
C(15)	0.6831(8)	0.6246(4)	0.4624(6)
H(1)	0.9195(56)	0.6923(39)	0.3722(51)
H(2)	0.9747(86)	0.8037(44)	0.2186(58)
H(3)	0.6047(60)	0.8563(31)	0.0465(44)
H(5)	0.5333(35)	0.7610(20)	0.3928(29)
H(6)	0.3433(36)	0.6565(22)	0.3706(31)
H(7)	0.4463(41)	0.6259(24)	0.1002(34)
H(8)	0.5105(44)	0.5076(22)	0.3132(34)
H(9A)	0.7717(44)	0.5410(26)	0.2366(37)
H(9B)	0.7109(59)	0.6041(29)	0.1306(41)
H(13A)	0.0664(42)	0.4796(24)	0.1559(36)
H(13B)	0.0819(43)	0.5811(29)	0.2257(38)
H(15A)	0.7826(67)	0.5809(39)	0.4618(51)
H(15B)	0.5674(64)	0.6009(32)	0.4737(51)
H(15C)	0.7132(59)	0.6784(32)	0.5090(47)

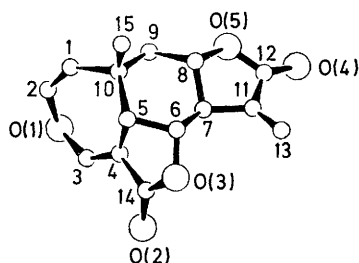
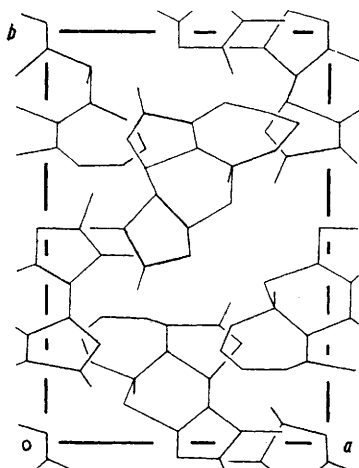


FIGURE 1 The atomic arrangement in the miscandenin molecule

FIGURE 2 The crystal structure viewed in projection along the *c* axis

displaced to opposite sides of the plane (see Table 6). While an exact description in terms of a simple ideal conformation is not feasible, the ring can be regarded as a very distorted flattened boat form in which C(1), C(2), C(4), and C(5) are roughly coplanar (to within $\pm 0.05 \text{ \AA}$)

TABLE 2

(a) Anisotropic thermal parameters * for the oxygen and carbon atoms ($\times 10^3$)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O(1)	213(9)	76(3)	249(8)	-75(9)	235(16)	-6(9)
O(2)	320(10)	45(2)	200(6)	39(8)	-247(14)	-4(6)
O(3)	109(5)	39(2)	163(4)	37(5)	-22(8)	-22(5)
O(4)	226(7)	48(2)	124(4)	-25(6)	-81(10)	-41(5)
O(5)	125(5)	38(1)	118(4)	8(5)	4(7)	-19(4)
C(1)	110(8)	70(4)	185(9)	-1(8)	-48(13)	-90(10)
C(2)	140(10)	66(4)	270(14)	-60(10)	107(22)	-115(14)
C(3)	231(13)	53(3)	134(7)	-48(10)	84(15)	-9(8)
C(4)	151(8)	31(2)	96(5)	-19(6)	21(11)	-7(5)
C(5)	89(5)	37(2)	73(5)	3(6)	2(9)	-16(5)
C(6)	96(6)	35(2)	89(5)	3(6)	13(9)	2(5)
C(7)	86(6)	31(2)	85(4)	8(5)	9(9)	6(5)
C(8)	93(6)	35(2)	86(5)	14(6)	-10(9)	-5(5)
C(9)	92(6)	40(2)	145(7)	31(6)	-11(12)	-17(7)
C(10)	107(7)	47(2)	107(5)	20(7)	-53(11)	-16(6)
C(11)	127(7)	36(2)	99(5)	-3(7)	-54(10)	6(6)
C(12)	149(8)	36(2)	88(5)	-11(7)	-38(10)	15(6)
C(13)	87(7)	63(3)	219(9)	-32(8)	13(13)	-26(11)
C(14)	150(8)	30(2)	129(6)	19(8)	-89(12)	-17(7)
C(15)	245(12)	69(3)	124(7)	45(11)	-185(17)	-4(8)

(b) Isotropic thermal parameters † (*B*) for the hydrogen atoms

H(1)	4.2	H(9A)	1.7
H(2)	6.8	H(9B)	3.0
H(3)	3.2	H(13A)	1.4
H(5)	1.1	H(13B)	2.0
H(6)	1.2	H(15A)	5.0
H(7)	1.1	H(15B)	4.7
H(8)	1.3	H(15C)	4.1

* In the form: $T = \exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$. † Mean standard deviation of isotropic temperature factors 0.9 \AA^2 .

TABLE 3

Intramolecular bonded distances (\AA), and standard deviations

O(1)-C(2)	1.389(11)	C(9)-C(10)	1.553(7)
O(1)-C(3)	1.337(9)	C(10)-C(15)	1.562(8)
O(2)-C(14)	1.203(7)	C(11)-C(12)	1.484(7)
O(3)-C(6)	1.456(5)	C(11)-C(13)	1.324(7)
O(3)-C(14)	1.356(6)	C(1)-H(1)	1.02(5)
O(4)-C(12)	1.193(6)	C(2)-H(2)	0.89(7)
O(5)-C(8)	1.459(5)	C(3)-H(3)	0.95(5)
O(5)-C(12)	1.363(6)	C(5)-H(5)	1.07(3)
C(1)-C(2)	1.296(11)	C(6)-H(6)	1.00(3)
C(1)-C(10)	1.508(7)	C(7)-H(7)	1.01(4)
C(3)-C(4)	1.325(8)	C(8)-H(8)	1.04(4)
C(4)-C(5)	1.486(6)	C(9)-H(9A)	0.95(4)
C(4)-C(14)	1.463(7)	C(9)-H(9B)	0.97(4)
C(5)-C(6)	1.546(6)	C(13)-H(13A)	1.01(4)
C(5)-C(10)	1.540(6)	C(13)-H(13B)	0.94(4)
C(6)-C(7)	1.519(6)	C(15)-H(15A)	1.08(6)
C(7)-C(8)	1.514(6)	C(15)-H(15B)	1.06(6)
C(7)-C(11)	1.491(6)	C(15)-H(15C)	0.97(5)
C(8)-C(9)	1.502(6)		

with O(1), C(3), and C(10) displaced by 0.17, 0.15, and 0.51 \AA to the same side of this plane. Angular strain is evident in the large valency angles at C(1) 133° , C(2) 132° , C(3) 131° , and C(4) 134° , the mean departure from

the ideal trigonal value being 12.3°. Dihydrodibenzoxepin rings are reported to have twist-boat conformations in several molecules.⁴

TABLE 4

Valency angles (deg.) and estimated standard deviations

C(3)-O(1)-C(2)	122.3(5)	C(11)-C(12)-O(4)	130.6(4)
C(4)-C(3)-O(1)	131.2(4)	C(9)-C(8)-O(5)	114.2(3)
C(4)-C(14)-O(2)	130.8(4)	C(11)-C(12)-O(5)	108.3(3)
C(5)-C(6)-O(3)	104.0(3)	C(10)-C(1)-C(2)	132.8(5)
O(5)-C(12)-O(4)	121.1(4)	C(9)-C(10)-C(1)	107.5(4)
C(12)-O(5)-C(8)	108.4(3)	C(5)-C(4)-C(3)	133.5(4)
C(7)-C(8)-O(5)	102.8(3)	C(14)-C(4)-C(5)	107.4(4)
C(5)-C(10)-C(1)	111.6(3)	C(6)-C(5)-C(4)	99.7(3)
C(15)-C(10)-C(1)	108.6(4)	C(10)-C(5)-C(6)	116.3(3)
C(14)-C(4)-C(3)	119.0(4)	C(7)-C(6)-C(5)	109.3(3)
C(10)-C(5)-C(4)	118.5(3)	C(15)-C(10)-C(5)	106.5(4)
C(9)-C(10)-C(5)	112.7(3)	C(11)-C(7)-C(6)	123.5(3)
C(8)-C(7)-C(6)	111.1(3)	C(11)-C(7)-C(8)	99.6(3)
C(13)-C(11)-C(7)	132.7(3)	C(9)-C(8)-C(7)	111.3(3)
C(1)-C(2)-O(1)	131.8(4)	C(12)-C(11)-C(7)	104.1(3)
O(3)-C(14)-O(2)	120.3(4)	C(10)-C(9)-C(8)	108.3(3)
C(14)-O(3)-O(6)	109.2(3)	C(15)-C(10)-C(9)	110.0(4)
C(7)-C(6)-O(3)	108.3(3)	C(13)-C(11)-C(12)	123.2(3)
C(4)-C(14)-O(3)	108.8(3)		

TABLE 5

Torsion angles (deg.)*

C(3)-O(1)-C(2)-C(1)	22	C(4)-C(5)-C(10)-C(1)	47
C(2)-O(1)-C(3)-C(4)	-6	C(4)-C(5)-C(10)-C(9)	-74
C(14)-O(3)-C(6)-C(5)	27	C(4)-C(5)-C(10)-C(15)	166
C(14)-O(3)-C(6)-C(7)	-89	C(6)-C(5)-C(10)-C(1)	166
C(6)-O(3)-C(14)-O(2)	173	C(6)-C(5)-C(10)-C(9)	45
C(6)-O(3)-C(14)-C(4)	-10	C(6)-C(5)-C(10)-C(15)	-76
C(12)-O(5)-C(8)-C(7)	-30	O(3)-C(6)-C(7)-C(8)	167
C(12)-O(5)-C(8)-C(9)	-151	O(3)-C(6)-C(7)-C(11)	-75
C(8)-O(5)-C(12)-O(4)	-173	C(5)-C(6)-C(7)-C(8)	54
C(8)-O(5)-C(12)-C(11)	7	C(5)-C(6)-C(7)-C(11)	172
C(10)-C(1)-C(2)-O(1)	2	C(6)-C(7)-C(8)-O(5)	172
C(2)-C(1)-C(10)-C(5)	-42	C(6)-C(7)-C(8)-C(9)	-66
C(2)-C(1)-C(10)-C(9)	82	C(11)-C(7)-C(8)-O(5)	40
C(2)-C(1)-C(10)-C(15)	-159	C(11)-C(7)-C(8)-C(9)	163
O(1)-C(3)-C(4)-C(5)	-2	C(6)-C(7)-C(11)-C(12)	-159
O(1)-C(3)-C(4)-C(14)	179	C(6)-C(7)-C(11)-C(13)	17
C(3)-C(4)-C(5)-C(6)	-151	C(8)-C(7)-C(11)-C(12)	-36
C(3)-C(4)-C(5)-C(10)	-24	C(8)-C(7)-C(11)-C(13)	141
C(14)-C(4)-C(5)-C(6)	27	O(5)-C(8)-C(9)-C(10)	178
C(14)-C(4)-C(5)-C(10)	154	C(7)-C(8)-C(9)-C(10)	62
C(3)-C(4)-C(14)-O(2)	-17	C(8)-C(9)-C(10)-C(1)	-174
C(3)-C(4)-C(14)-O(3)	166	C(8)-C(9)-C(10)-C(5)	-51
C(5)-C(4)-C(14)-O(2)	164	C(8)-C(9)-C(10)-C(15)	68
C(5)-C(4)-C(14)-O(3)	-13	C(7)-C(11)-C(12)-O(4)	-160
C(4)-C(5)-C(6)-O(3)	-32	C(7)-C(11)-C(12)-O(5)	19
C(4)-C(5)-C(6)-C(7)	83	C(13)-C(11)-C(12)-O(4)	23
C(10)-C(5)-C(6)-O(3)	-161	C(13)-C(11)-C(12)-O(5)	-158
C(10)-C(5)-C(6)-C(7)	-45		

* The sign convention is such that the sign is negative if an anticlockwise rotation is required of atom (1) to eclipse atom (4) whilst looking down the (2)-(3) bond. Mean standard deviation of torsion angle 0.6°.

The cyclohexane ring adopts a somewhat distorted chair conformation in which atoms C(6), C(7), C(9), and C(10) are closely coplanar and atoms C(5) and C(8) are displaced by -0.54 and 0.72 Å from this plane.

⁴ H. Shimanouchi, Y. Sasada, T. Honda, and T. Kametani, *J.C.S. Perkin II*, 1973, 1226; T. Kametani, S. Shibuya, and W. D. Ollis, *J. Chem. Soc. (C)*, 1968, 2877.

⁵ Mazhar-Ul-Haque and C. N. Caughlan, *J. Chem. Soc. (B)*, 1967, 355

⁶ T. A. Dullforce, G. A. Sim, D. N. J. White, J. E. Kelsey, and S. M. Kupchan, *Tetrahedron Letters*, 1969, 973.

The α,γ -fused lactone at C(4)-(6) has a slightly distorted half-chair conformation; C(5) is displaced by 0.31 and C(6) by -0.23 Å from the plane defined by atoms O(3), C(4), and C(14). The β,γ -fused lactone at C(7)-(8) approximates more closely to an envelope form in which C(7) is the out-of-plane atom, for C(7) is

TABLE 6

Displacements (Å) of atoms from various planes. Atoms not included in the derivation of a plane are italicized

(1): C(1) -0.06, C(2) 0.05, C(4) -0.04, C(5) 0.05, O(1) -0.17, C(3) -0.15, C(10) -0.51

(2): O(1) 0.00, C(3) -0.01, C(4) 0.01, C(5) 0.00, C(1) -0.06, C(2) 0.15, C(10) -0.59

(3): O(1) 0.00, C(2) -0.01, C(1) 0.01, C(10) 0.00, C(3) 0.45, C(4) 0.86, C(5) 0.93

(4): C(6) 0.01, C(7) -0.01, C(9) 0.01, C(10) -0.01, C(5) -0.54, C(8) 0.72

(5): O(3) 0.00, C(4) 0.00, C(14) 0.00, C(5) 0.31, C(6) -0.23

(6): O(5) 0.00, C(11) 0.00, C(12) 0.00, C(7) -0.47, C(8) 0.18

TABLE 7

Intermolecular contacts < 3.85 Å

O(3) ... C(2 ^{VI})	3.502	O(2) ... O(5 ^{VI})	3.466
C(6) ... O(4 ^{III})	3.280	O(2) ... C(8 ^{VI})	3.429
C(13) ... O(4 ^{III})	3.754	O(2) ... C(9 ^{VI})	3.805
O(5) ... C(15 ^{III})	3.358	C(1) ... O(4 ^{VI})	3.500
O(1) ... O(2 ^{IV})	3.483	C(2) ... O(4 ^{VI})	3.572
O(1) ... O(3 ^{IV})	3.690	C(3) ... O(4 ^{VI})	3.776
O(1) ... C(7 ^{IV})	3.464	C(3) ... O(5 ^{VI})	3.649
O(1) ... C(11 ^{IV})	3.600	C(3) ... C(12 ^{VI})	3.547
O(1) ... C(14 ^{IV})	3.466	C(4) ... O(4 ^{VI})	3.495
C(3) ... O(2 ^{IV})	3.790	C(4) ... O(5 ^{VI})	3.273
C(3) ... O(3 ^{IV})	3.843	C(4) ... O(12 ^{VI})	3.438
C(3) ... C(11 ^{IV})	3.680	C(5) ... O(4 ^{VI})	3.292
C(3) ... C(13 ^{IV})	3.709	C(5) ... O(5 ^{VI})	3.700
C(9) ... O(2 ^{IV})	3.501	C(5) ... C(12 ^{VI})	3.704
O(3) ... C(15 ^V)	3.817	C(10) ... O(4 ^{VI})	3.822
O(1) ... C(12 ^{VI})	3.841	C(14) ... O(5 ^{VI})	3.311
O(1) ... C(13 ^{VI})	3.845	C(14) ... C(8 ^{VI})	3.743

Roman numeral superscripts refer to the following transformations of the atomic co-ordinates:

I $x - 1, y, z$	IV $x + \frac{1}{2}, -y + \frac{3}{2}, -z$
II $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$	V $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$
III $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$	VI $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$

displaced by -0.47 and C(8) by 0.18 Å from the plane defined by O(5), C(11), and C(12). γ -Lactones with exocyclic methylene groups are conformationally rather variable, e.g. in bromomexicanin-E⁵ and bromogailardin⁶ envelope conformations are displayed, in euparotin *p*-bromobenzoate⁷ and elephantol *p*-bromobenzoate⁸ roughly planar conformations are found, and in vernolepin *p*-bromobenzenesulphonate⁹ and berlandin¹⁰ the γ -lactones adopt half-chair conformations.

A survey of several X-ray analyses has revealed that

⁷ A. T. McPhail and G. A. Sim, *Tetrahedron*, 1973, 29, 1751.

⁸ A. T. McPhail and G. A. Sim, *J.C.S. Perkin II*, 1972, 1313.

⁹ A. T. McPhail and G. A. Sim, *J. Chem. Soc. (B)*, 1971, 198.

¹⁰ P. J. Cox, Ph.D. Thesis, University of Glasgow, 1972.

the C(α)-C(β)-C(γ)-O and C=C=O torsion angles in $\alpha\beta'$ -unsaturated γ -lactones have paired signs with the former angle having *ca.* twice the magnitude of the latter.⁷ Both lactone rings in miscandenin conform to this pattern, C(11)-C(7)-C(8)-O(5) being 40° and C(13)-C(11)-C(12)-O(4) 23°, while C(4)-C(5)-C(6)-O(3) is -32° and C(3)-C(4)-C(14)-O(2) -17°. This general conclusion is relevant to the study of the c.d. and o.r.d. spectra of sesquiterpenoid α -methylene γ -lactones, since the sign of the Cotton effect of the $n \rightarrow \pi^*$ transition has been related both to the chirality of the C=C-C=O chromophore and to the ring-junction position and stereochemistry.¹¹

EXPERIMENTAL

Crystal Data.—C₁₅H₁₄O₅, $M = 274.3$. Orthorhombic, $a = 8.586(4)$, $b = 14.918(5)$, $c = 10.211(3)$ Å, $U = 1307.8$ Å³, $D_m = 1.37$, $Z = 4$, $D_c = 1.39$, $F(000) = 576$. Mo- K_α radiation, $\lambda = 0.7107$ Å; $\mu(\text{Mo-}K_\alpha) = 1.14$ cm⁻¹. Space group $P2_12_12_1$ (D_2^4).

Crystallographic Measurements.—Cell dimensions were adjusted by least-squares treatment of θ values for 12 reflections, measured with Mo- K_α radiation (at *ca.* 16°) on a Hilger and Watts automatic diffractometer. For intensity measurements the octant hkl was scanned out to $\theta \leq 27^\circ$ by means of $\theta-\omega$ scans which consisted of 40 steps of 0.02° s⁻¹. Background counts were taken at each end of the scan range for 15 s. In all, 1639 independent reflections were surveyed, of which 1222, having $I > 2\sigma(I)$, were considered observed. No absorption correction was applied.

Structure Analysis.—The crystal structure was elucidated by direct phase-determining methods using the 'X-Ray '70' series of programmes.¹² $|E|$ values were calculated based on an overall temperature factor $B = 3.65$ Å² and Σ_2 relationships were generated for the 184 reflections with $|E| \geq 1.50$. The initial set of phases consisted of three origin-determining phases,¹³ a suitable enantiomorph-

determining phase, and two additional phases to which values of $\pm\pi/4$, $\pm 3\pi/4$ were given (Table 8; see Supplementary Publication). This procedure gave sixteen possible starting sets of six phases for input to the 'Tangen' programme. The resulting R_K range¹⁴ was 0.19–0.32.

An E -map generated from the phase set characterized by R_K 0.19 yielded the correct solution; from this map the positions of almost all the carbon and oxygen atoms, apart from two atoms of the dihydro-oxepin ring and the methyl carbon, were located. An initial structure-factor calculation gave R 54.1% and after one cycle of least-squares adjustment a Fourier difference map revealed the positions of the missing carbon atoms.

Reflections for which $I \leq 2\sigma(I)$ were now removed from the calculations and the atoms allowed to refine isotropically in calculations which reduced R to 14.0%. Subsequent anisotropic refinement converged at R 10.4%, at which stage a difference electron-density distribution revealed all the hydrogen sites. The hydrogen atoms were then included in the calculations with isotropic temperature parameters and convergence was reached at R 7.0%, R' 6.6%. The weighting scheme used in the final cycles of least-squares calculations was of the form $w = 1/[1 + (F_O - F_B)/F_A]^2$, final values of F_A and F_B being 4.44 and 9.48. The mean and maximum shift-to-error ratios in the last cycle of calculations were 0.11 and 0.49, respectively. No allowance was made for anomalous dispersion in any of the calculations and the absolute configuration adopted for (1) is based² on the correlation of deoxymikanolide with the germacranolides isabelin and cnicin. Observed and calculated structure amplitudes, together with Table 8, are included in Supplementary Publication No. SUP 21057 (9 pp.).*

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1973, Index issue.

¹¹ W. Stöcklin, T. G. Waddell, and T. A. Geissman, *Tetrahedron*, 1970, **26**, 2397; A. F. Beecham, *ibid.*, 1972, **28**, 5543.

¹² 'X-Ray '70' series of programs, July 1970 version, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland.

¹³ H. Hauptman and J. Karle, *Acta Cryst.*, 1956, **9**, 45.

¹⁴ J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.